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(Cr-Fe)N coatings deposited on X10CrNiTi 18 10 steel by magnetron sputtering in a vacuum furnace*

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(Cr-Fe)N coatings are deposited on X10CrNiTi 18 10 steel substrates by magnetron sputtering, of a ferrochromium target in a single-chamber vacuum furnace. The experiments are carried out in the temperature interval 450 - 850 °C in a gaze mixture of Ar + N₂ at a pressure of 6 – 7x10⁻³ mbar. The chemical and phase compositions of the coatings, their lattice parameter and texture are determined by XRD, GDOES and an electron probe X-ray methods. The microhardness also has been investigated.

1. INTRODUCTION

The CrN coatings are analogous by structure and properties to the TiN coatings and even exceed them in some aspects.[1, 2, 3]. Lately a great interest has been pointed to the multicomponent (Cr-Me)N coatings due to their extreme properties. They contain additional metals (usually one or two) like Ti, Al, W, Mo, Nb, Ta [4, 5, 6] and are obtained by PVD units equipped with several vapor sources – magnetrons or arc evaporators. This units have a high price, necessity of precise simultaneous control on the vapor sources, composition inhomogeneity of the coatings deposited at different points in the metallizing chamber etc. In this regard it is of interest to obtain (Cr-Me)N coatings by magnetron sputtering of alloyed targets containing additional metals except Cr. The technical ferrochromium alloys which composition is about 60 wt. %Cr, 1 - 2 wt. %Si, 0,01 - 8 wt. %C, impurities (Al and others) – up to 0,5 wt. % and Fe – the rest are suitable for this purpose. They are available and cheap. The coatings can be obtained diffusively bonded to the substrate using a new-developed method – *PVDM* [9]. The process is carried out in a vacuum furnace with a built-in DC magnetron and graphite heating and isolative components. In many cases of the practice the working surfaces of parts made of stainless austenite steels are required to be hard and wear-resistant without lessening their corrosion resistance. This requirement can be satisfied either

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by nitriding at a comparatively low temperatures – even in-between 350 - 450°C [13] or by surface diffusive saturation with Cr at high temperatures – about 1000°C [14]. Both types of processes are carried out in specialized vacuum furnaces.

In connection with the above-said the aim of the work is to study the possibility to obtain (Cr-Fe)N coatings diffusively bonded to the substrates of austenite steel by magnetron sputtering of a technical ferrochromium alloy in a vacuum furnace.

2. EXPERIMENTAL PROCEDURE

The coatings have been deposited in a single-chamber vacuum furnace with a built-in DC magnetron [7] on substrates of X10CrNiTi 18 10 stainless steel (<0,08 at. %C, 17 – 19 at. %Cr, 8 – 11 at. %Ni, <2,0 at. %Mn, <0,3 at. %Mo and ~ 0,7 at. %Ti). Reaching an initial vacuum of $6 - 8 \times 10^{-4}$ mbar in the chamber they have been heated to the metallizing temperature $T_M = 450, 500, 550, 600, 650$ and 850°C . Then the substrates have been cleaned by glow discharge in Ar at a pressure of 2×10^{-1} mbar for 5 min at 900 V. A target of FeCrC010 alloy (60 wt. %Cr, 1,5 wt. %Si, 0,1 wt. %C, 0,3 wt. %Al, 0,03 wt. %P, 0,03 wt. %S and Fe – the rest) has been sputtered at a pressure of $6 - 8 \times 10^{-3}$ mbar in a mixture of Ar ($G_{Ar} = 3,5$ sccm) and N_2 ($G_N = 26$ sccm) for 60 min at a sputtering power of 2 kW ($I_{sp} = 5$ A) and a substrate bias $U_s = 0$ V. The condensation rates have been $V_c = 0,08$ and $0,18$ $\mu\text{m}/\text{min}$ for a target-to-substrate distance $L_{t-s} = 70$ and 95 mm. The chemical composition has been determined by GDOES on a Leco 750GDS instrument and by an electron probe X – ray microanalyzer JXA 733 on a SEM JEOL SUPERPROBE 733. The phase composition, structure, texture and lattice parameter of the coatings have been studied metallographically and by XRD method using FeK_α radiation. The microhardness has been measured by a Vickers nanoindentation tester FISCHERSCOPE[®] H100 using a load of 50 mN.

3. RESULTS AND DISCUSSIONS

Appearance, topography and structure. The coatings have a gray color getting darker one when increasing T_M . According to [11] the bulk CrN phase is black whereas the vacuum obtained CrN coatings are considered to have a light gray color which passes into black one in a degree depending on the oxygen content in the vacuum chamber. In the case this is due to the graphite components which diminishes this content. After the topography studies (at magnifications x500 and over) the coatings are built of grains growing up when increasing T_M . This tendency is well-defined at $T_M = 650 - 850^\circ\text{C}$ – they grains form larger ones with delineated boundaries. The topography permits the coatings obtained at $T_M < 600^\circ\text{C}$ to be assigned to Zone II of the Thornton's Zone Model [10] whereas the others belong to Zone III. For the coatings present here the boundary between the zones is shifted to the higher temperatures ($T_M/T_{\text{melting}} = 0,6 - 0,7$) than that in the model ($T_M/T_{\text{melting}} = 0,5$). This is due to the complicated refractory phases in them (nitrides and carbides) which have higher recrystallization temperatures [12] causing the bulk diffusion in Zone III. The observation of the structure on a cross section shows a presence of a diffusive interaction between the coating and substrate. The nitrogen penetrates into the substrate predominantly along the grain boundaries and preferable crystallographic directions in them (Fig. 1).

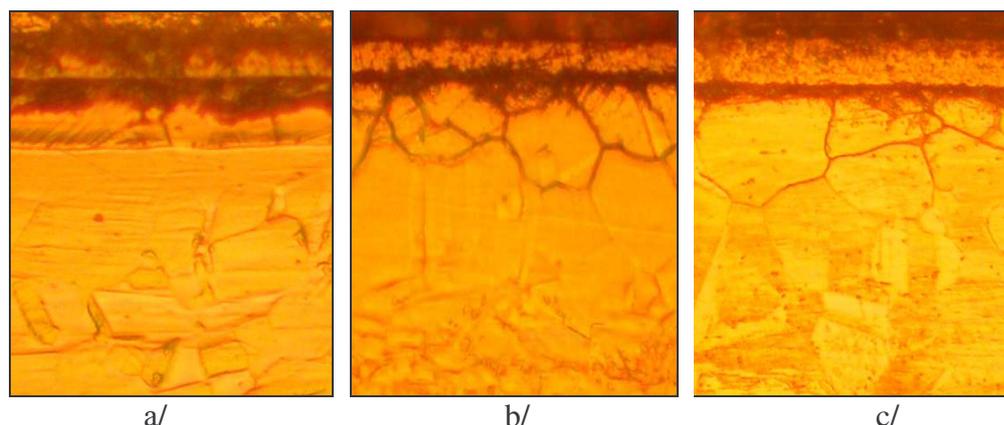


Figure 1. Microstructure (x700) of (Cr-Fe)N coatings deposited on X10CrNiTi 18 10 steel at: a) $T_M = 450^\circ\text{C}$ $L_{t-s} = 70$ mm, b) $T_M = 850^\circ\text{C}$ $L_{t-s} = 95$ mm, c) $T_M = 850^\circ$ $L_{t-s} = 70$ mm.

Chemical and phase composition. The X – ray microanalyzer data of the coatings show a presence of Cr, Fe, Si, Ni, Mn, N and C. Due to the predominant quantities of Cr and Fe the coatings and phases are signed (Cr, Fe) based ones. When increasing T_M the total quantity of N in the coatings obtained at $L_{t-s} = 70$ mm decreases from 45 at. % to 37 at. % and from 43 at. % to 25 at. % for those obtained at $L_{t-s} = 95$ mm. In parallel to this the Cr and C contents increase whereas the rest elements have constant quantities for the both L_{t-s} . The XRD analyses have found the following phases: (Cr,Fe)N, (Cr,Fe)₂N, (Cr,Fe)₂CN and α (Cr,Fe) and γ (Cr,Fe) solid solutions from the substrate.

The GDOES analysis gives more detailed information. The studies are pointed to the coatings deposited at $L_{t-s} = 95$ mm because the overheating of the substrate surface layer is smaller and hence, the actual temperature of a diffusive interaction is closer to the measured T_M . The nitrogen penetration into the substrate is intensive still in the interval $T_M = 450 - 600^\circ\text{C}$ and is co-measurable by rate with the condensate growth. This leads to a partial change of the (Cr,Fe)N phase into (Cr,Fe)₂CN one during the deposition process. Therefore, according to the *General Model for Vacuum Condensates and Vacuum Diffusive Coatings* [9] it is formed not a condensate but a zone (or an underlayer) of a substrate diffusion into the coating $\delta_{s \rightarrow c}$. Due to the small thickness of the coatings there exists no residual condensate because Zone I (Fig. 2a) displays a ratio metal to metalloid atoms nearly 1 : 1. This is caused by the secondary interaction between the coating and the residual atmosphere during its cooling after the deposition process. The nitrogen in the $\delta_{s \rightarrow c}$ zone diminishes towards the substrate which speaks for a change of the ratio between the (Cr,Fe)N and (Cr,Fe)₂CN phases and also for a gradual disappearance of the former when reaching the initial boundary coating–substrate. In the next zone $\delta_{c \rightarrow s}$ (a zone of a coating diffusion into the substrate) the nitrogen concentration reaches 22 – 25%. In depth it follows the diffusive influence zone (DIZ). The phases content is higher and it is easier to find them metallographically (Fig. 1). When increasing T_M (Cr,Fe)N gradually turns into (Cr,Fe)₂CN at 600°C because the saturation with carbon also increases during the process. This result classifies the coating as a vacuum diffusive coating (VDC) still in the interval 450 - 600°C for the used V. The character and type of the coating can be defined by the coefficient of diffusiveness K_{Dc} [9]. It is the relation of the thickness of the diffusive part signed as TDL - transitional diffusive layer ($\delta_{TDL} = \delta_{s \rightarrow c} + \delta_{c \rightarrow s}$) to the total thickness (δ_c) of the whole coating. In the case $K_{Dc} \rightarrow 1$.

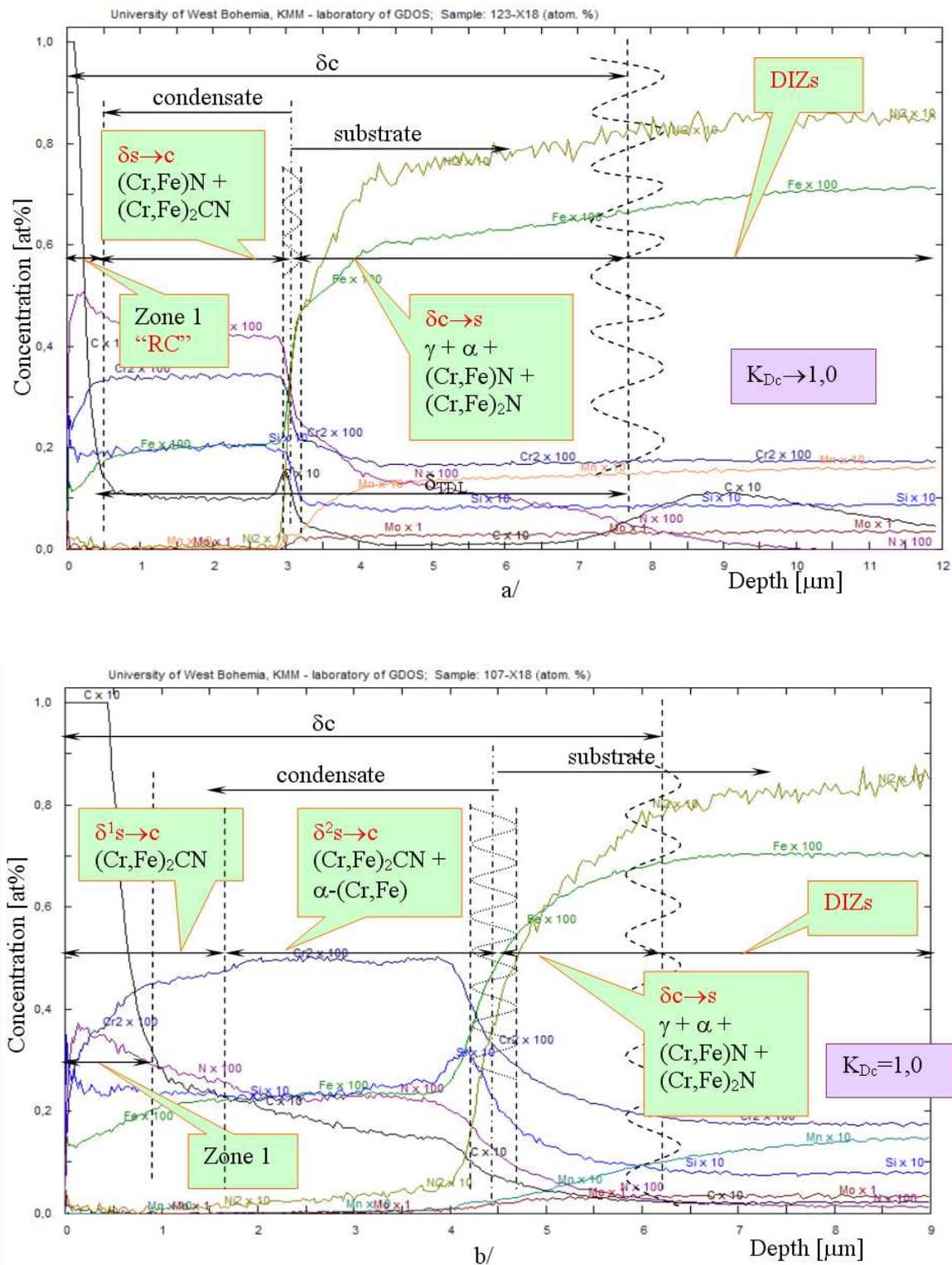


Figure 2. GDOES profiles of (Cr-Fe)N coatings deposited on X10CrNiTi 18 10 steel at: a) $T_M = 450^\circ\text{C}$ $L_{t-s} = 95$ mm, b) $T_M = 850^\circ\text{C}$ $L_{t-s} = 95$ mm.

The farther increase of T_M lowers the nitrogen quantity in the both underlayers - $\delta_{s \rightarrow c}$ and $\delta_{c \rightarrow s}$. That is why the (Cr,Fe)N quantity in $\delta_{s \rightarrow c}$ diminishes and at the boundary coating – substrate disappears in practice while the $\delta_{c \rightarrow s}$ underlayer, situated in the substrate, gets thinner. The maximum nitrogen concentration in it reaches about 10 at. %. The diffusion of nitrogen into the substrate accelerates still farther at 850°C. It causes a disappearance of the (Cr,Fe)N phase in $\delta_{s \rightarrow c}$ and an appearance of $\alpha(\text{Cr,Fe})$ at the side of the substrate (Fig. 2 b). The ferrite formation is also promoted by the redistribution of Cr and Ni between the condensate and substrate which arouses a partial $\alpha \leftrightarrow \gamma$ transformation. As a result of this $\delta_{s \rightarrow c}$ divides into two underlayers. The first one ($\delta_{s \rightarrow c}^1$) built of $(\text{Cr,Fe})_2\text{CN}$ is situated at the outer side towards the coating surface whereas the second one ($\delta_{s \rightarrow c}^2$) built of $(\text{Cr,Fe})_2\text{CN} + \alpha(\text{Cr,Fe})$ lies towards the substrate. For these coatings $K_{DC} = 1$. The diffusive interaction between the condensate and substrate at 850°C is active enough for VDCoatings without RC having a bigger thickness (for instance 20 μm) to be obtained.

The forming of (Cr-Fe)N coatings on stainless steels of the type 18-10 is more intensive than the forming of CrN ones still at 450°C probably due to a lower energy of the atom bonds in the nitride phase alloyed with Fe. This makes the appliance of a negative bias more expedient in the case of solid substrates. It will cause an overheating only of their surface layers and therefore will intensify in addition the diffusive interaction without a needless dissipation of the nitrogen in depth of the substrate.

Texture, lattice parameter and hardness. In work the “C-axes” texture has been studied by a method proposed in [8]. The calculations have been made for the main phase in the coatings (Cr,Fe)N. The coatings obtained at $T_M = 450 - 600^\circ\text{C}$ have a well-expressed texture according to $\langle 200 \rangle$ with a maximum at 500°C for the both distances L_{t-s} . After that it decreases and over 650°C the predominant texture disappears owing to the equistatistical orientation of the grains caused by the recrystallization processes. The deviation of the lattice parameter a_0 calculated according to the $\langle 200 \rangle$ axis is well-defined and depends on T_M . The deviation is largest in the interval 450 - 600°C and diminishes to a constant value for the higher temperatures. It is clear that $a_0(200)$ will remain less than the theoretical one, even at a stoichiometric composition of the phase. This is due to the metal impurities Fe, Si, Ni which atom diameters are less than that of the chromium and cause a shrinkage of the lattice. Probably the higher T_M leads to a more uniform distribution of the impurities in the lattice. The hardness is highest in the above mentioned T_M interval (1100 – 1400HV) and lowers to comparatively constant values of 700 – 1000HV when increasing T_M . The result is due to the predominant texture $\langle 200 \rangle$ and the high level of stresses and defects which decrease and disappear at the highest temperatures.

4. CONCLUSIONS

1. The coatings as obtained have a grey colour getting darker when increasing T_M . According the topography and microstructure these obtained in the interval $450 \div 600^\circ\text{C}$ belong to the Zone II of The Thornton's Zone Model whereas the others obtained at higher T_M correspond to the Zone III of the Model.

2. All the coatings can be classified as vacuum diffusive coatings without a residual condensate. Their coefficient of diffusiveness is $K_{DC} = 1$.

3. The samples obtained at $T_M = 450 \div 650^\circ\text{C}$ are double-layered. The outer underlayer $\delta_{s \rightarrow c}$ is the zone of a substrate diffusion into the coating and is built of $(\text{Cr,Fe})\text{N} + (\text{Cr,Fe})_2\text{CN}$. The inner one $\delta_{c \rightarrow s}$ lies in the substrate. It is the zone of a coating diffusion into the substrate

and consists of $(\text{Cr,Fe})\text{N} + (\text{Cr,Fe})_2\text{CN} + \alpha(\text{Cr,Fe}) + \gamma(\text{Cr,Fe})$. At the coatings obtained at 850°C due to the active diffusive interaction between the condensate and the substrate the $\delta_{s \rightarrow c}$ underlayer divides into two parts. The first one ($\delta_{s \rightarrow c}^1$) built of $(\text{Cr,Fe})_2\text{CN}$ is situated at the outer side towards the coating surface whereas the second one ($\delta_{s \rightarrow c}^2$) built of $(\text{Cr,Fe})_2\text{CN} + \alpha(\text{Cr,Fe})$ lies towards the substrate.

4. The texture, lattice parameter and hardness of the coatings are in a good correlation among them and strongly depend on T_M . Their essential changes occur in the interval $600 \div 650^\circ\text{C}$ with the start of the active diffusion of the metals atoms and recrystallization processes.

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